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Oxidation and thermal reduction of the Cu(1 0 0) surface as studied using positron annihilation induced Auger electron spectroscopy (PAES)

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ABSTRACT

Changes in the surface of an oxidized Cu(1 0 0) single crystal resulting from vacuum annealing have been investigated using positron annihilation induced Auger electron spectroscopy (PAES). PAES measurements show a large increase in the intensity of the annihilation induced Cu $M_{2,3}VV$ Auger peak as the sample is subjected to a series of isochronal anneals in vacuum up to annealing temperature 300 °C. The intensity then decreases monotonically as the annealing temperature is increased to ~600 °C. Experimental probabilities of annihilation of surface-trapped positrons with Cu *3p* and O *1s* core-level electrons are estimated from the measured intensities of the positron annihilation induced Cu $M_{2,3}VV$ and O KLL Auger transitions. Experimental PAES results are analyzed by performing calculations of positron surface states and annihilation probabilities of surface-trapped positrons with relevant core electrons taking into account the charge redistribution at the surface, surface reconstructions, and electron–positron correlations effects. The effects of oxygen adsorption on localization of positron surface state wave function and annihilation characteristics are also analyzed. Possible explanation is proposed for the observed behavior of the intensity of positron annihilation induced Cu $M_{2,3}VV$ and O KLL Auger peaks and probabilities of annihilation of surface-trapped positrons with Cu *3p* and O *1s* core-level electrons with changes of the annealing temperature.

1. Introduction

The understanding of metals oxidation is of both fundamental and practical importance in a wide variety of applications from corrosion to catalysis. Copper has received much attention due to the use of copper and its oxides in catalytic applications. In particular, many studies have been prompted by the use of copper in methanol synthesis catalysts [1] and to a lesser degree for the possible use in zeolite catalysts for the reduction of NO by CO in relation to automotive catalytic converters [2,3]. Under catalytic operating conditions or during activation, the copper component of catalysts may be modified on exposure to oxidizing and reducing environments. For example, partial surface reduction of Cu_2O single crystal surfaces to Cu has been observed by dosing with acrolein [4]. The reduction was attributed to consumption of lattice oxygen to burn off hydrogen and surface carbon. An investigation of the oxidation and reduction behavior of copper oxides could therefore be of catalytic interest. Furthermore, modifications of surface composition easily accessible under ultra-high vacuum (UHV) conditions are of clear importance to the preparation of copper oxide surfaces for surface science studies. Several investigations have been carried out into the oxidation and reduction behavior of copper oxides using surface science techniques [5–14].

Recently the novel surface characterization technique, positron annihilation induced Auger electron spectroscopy (PAES), has been used to study the effects of adsorption of oxygen on metal and semiconductor surfaces on changes to their properties [15]. PAES uses a low energy beam to place positrons into an image-correlation well at the surface. A few percent of the positrons trapped in this well annihilate with core electrons resulting in highly excited atoms that relax via the emission of Auger electrons. Because the core holes are created via matter–antimatter annihilation, PAES spectra can be obtained by using very low incident beam energies (~15 eV). Unlike conventional Auger techniques that average over several atomic layers, PAES has a very high degree of top layer selectivity due to the fact that the positrons are trapped just outside the surface prior to annihilation, hence is ideal to probe the near surface region and study the initial stages of oxidation [16,17].

In this paper we present the results of studies of the oxidation and reduction behavior of copper oxide using PAES. In the experiments reported here, the oxide layer was formed by exposing the

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